

May 31, 1883.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

THE BAKERIAN LECTURE—"On Radiant Matter Spectroscopy. A New Method of Spectrum Analysis," was delivered by WILLIAM CROOKES, F.R.S. Received May 24, 1883.

The following is an Abstract :—

For several years I have been examining the phenomena presented by various substances when struck by the molecular discharge from the negative pole in a highly exhausted tube. I have ventured to call this discharge "radiant matter," and under its influence a large number of substances emit phosphorescent light, some faintly and others with great intensity. On examining the emitted light in the spectroscope most bodies give a faint continuous spectrum, with a more or less decided concentration in one part of the spectrum, the superficial colour of the phosphorescing substance being governed by this preponderating emission in one or other part of the spectrum. Sometimes, but more rarely, the spectrum of the phosphorescent light is discontinuous, and it is to bodies manifesting this phenomenon that my attention has been specially directed.

For a long time past I have been haunted by a bright citron-coloured band or line appearing in these phosphorescent spectra, sometimes as a sharp line, at others as a broader nebulous band, but having always a characteristic appearance and occurring uniformly in the same spot. The best way to bring out the band is to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to redness. The anhydrous sulphate thus left frequently shows the citron band in the radiant matter tube, when before this treatment the original substance shows nothing. I soon came to the conclusion that the substance I was in search of was an earth, but on attempting to determine its chemical properties I was baffled.

Much chemical evidence tended to support the view that the band might be due to a compound of lime. By neglecting the portion showing least citron band, and separating all the elements present which gave little or none, I could generally concentrate the citron band into a solution which—according to our present knowledge of analytical chemistry—should contain little else than the earths,

alkaline earths, and alkalis. Ammonia added to this solution would precipitate an earth, and in the filtrate oxalic acid would precipitate an insoluble oxalate, showing the citron band strongly. This was found on analysis to consist of strontic and calcic oxalates. The strontia being separated, the remaining lime formed an oxalate which gave the citron band.

So far all the chemical evidence went to show that the band-forming substance was calcium, and further tests tried with the purified oxalate confirmed this inference. Every analytical test to which it was subjected showed lime, and nothing but lime; all the salts which were prepared from it resembled those of lime, both physically and chemically; the flame spectrum gave the calcium lines with extraordinary purity and brilliancy; and, finally, the atomic weight, taken with great care, came out almost the same as that for calcium, 39.9 as against Ca 40.

On further examination it was found that most native compounds of lime gave the citron band. It was found in clear and colourless Iceland spar, native calcic phosphate, a crystal of arragonite, a stalactite of calcic carbonate from Gibraltar, cinnamon stone (lime alumina garnet), iron slag from a blast-furnace, pink coral, commercial plaster of Paris, and most specimens of ordinary burnt lime.

Evidence stronger than this in favour of the view that the citron band was an inherent characteristic of calcium could scarcely be; but, on the other hand, there was evidence equally conclusive that the band was not essential to calcium.

Starting with a lime compound which showed the citron band, I could always obtain a calcic oxalate which gave the band stronger than the original substance; but if I started with a lime compound which originally gave no citron band, I could never by any means, chemical or physical, constrain the lime or the earthy precipitate to yield a citron band.

The only explanation that I could see for this anomaly was that the elusive citron band was caused by some element precipitated with the calcic oxalate, but present in a quantity too small to be detected by ordinary chemical means. The calcic oxalate was ignited and dissolved in hydrochloric acid, and fractionally precipitated in three portions with ammonic oxalate, the first and third portions being comparatively small. They were then tested in the radiant matter tube. All three portions showed the citron band, but the portion which came down first gave the band decidedly the strongest, and the third portion precipitated showed it weakest.

It having been found that the substance giving the citron band formed a sulphate more soluble in water than calcic sulphate, 4 lbs. weight of commercial plaster of Paris, which showed very faint traces of the citron band, were mixed with water and poured on

a large filter. A few ounces of water were poured on, and after passing through, poured back, and the exhaustion repeated several times. The aqueous extract was then evaporated to dryness, ignited with sulphuric acid, ground in a mortar with small successive quantities of water, and precipitated with ammoniac oxalate. The precipitate, ignited with sulphuric acid, showed the citron band very fairly, far more intensely than it was seen in the original calcic sulphate.

These experiments are conclusive in proving that the citron band is not due to calcium, but to some other element, probably one of the earthy metals, occurring in very minute quantities but widely distributed along with calcium, and I at once commenced experiments to find a more abundant supply of the body sought for. Amongst other substances tested I may note the following as giving a more or less decided citron band in the spectrum when treated with sulphuric acid in the manner indicated above:—Crystallised barytic chlorate, heavy spar, common limestone, strontic nitrate, native strontic carbonate, crystallised uranic nitrate, commercial magnesian sulphate, commercial potassic sulphate, tobacco ash, wagnerite (magnesian phosphate and fluoride), zircon, cerite, and commercial ceric oxalate.

Some specimens of zircon appeared sufficiently rich to make it probable that here might be found an available source of the citron band yielding body. I found it in crystals from Green River, North Carolina, from Ceylon, from Expailly, from Miask (Ural), and from Brevig, and having a good supply of North Carolina zircons, these were worked up by a process given in detail in the paper.

I may condense a year's work on zircon,—over 10 lbs. weight of crystals from North Carolina having been worked up—by stating that the result was comprised in about 300 grs. of an earthy residue, and about 2 ozs. of oxalate, chiefly calcic; the former gave the citron band very well.

The zirconia prepared from these zircons, when tested, sometimes showed the citron band, and at other times none. A zirconia rich in citron band, fractionally precipitated by ammonia, yielded precipitates of increasing richness, the last fraction showing the citron band strongly.

The calcic oxalate obtained from zircon gave unsatisfactory results, so attention was directed to the earthy residue. This was found to be of highly complex character, containing thorium, cerium, lanthanum, didymium, yttrium, and probably some of the newly-discovered rarer earths.

The position of the citron band in the spectrum falls exactly on the strongest absorption band of didymium, so that a piece of didymium glass or cell of solution of the nitrate entirely obliterates the citron band. This naturally suggested that the band was due to didymium.

Cerite was accordingly the next mineral experimented on. The powdered mineral tested in the tube in the original way gave a good citron band. The mixed earths after extraction were converted into sulphates, dissolved in water, and the cerium metals precipitated by long digestion with excess of potassic sulphate.

The precipitated double sulphates were converted into oxalates, and after ignition and treatment with sulphuric acid, the mixed ceria, lanthana, and didymia were tested in the radiant matter tube, but the merest trace only of citron band was visible.

This experiment proved the inadequacy of the didymium explanation, and further tests showed that not only could I get no citron band in pure didymium compounds, but the spectrum entirely failed to detect didymium in many solutions of the earth which gave the citron band brilliantly.

Attention was now turned to the solution filtered from the insoluble double sulphates. Potash was added, and the precipitate filtered off, and tested in a radiant matter tube. The spectrum, of extraordinary brilliancy, was far brighter than any I had hitherto obtained. Unfortunately, however, the quantity was too small to be subjected to very accurate chemical analysis.

Search was now made amongst other minerals rich in the rarer earths. Thorite was finely powdered, treated with sulphuric acid, and tested in the radiant matter tube. It gave the citron spectrum most brilliantly—equal in fact to the mixture of earths obtained from zircons at so great an expenditure of time and trouble. Orangite treated in the same manner gave almost as good a spectrum. Pure thorinic sulphate prepared by myself was found not to give the citron band, but three specimens prepared and given to me by friends all gave it, so it was not unlikely that in thorite and orangite might at last be found a good source of the long-sought element—that in fact the body I was hunting for, if not thorina, might possibly be Bahr's hypothetical wasium. Two pounds of orangite and thorite were extracted with hydrochloric acid. The solution was precipitated with potassic sulphate, taking the usual precautions to secure complete precipitation. A bulky precipitate ensued, which contained the thorina and cerium earths. These were separated and tested, and found to give only a faint citron band.

The solution of earthy sulphates soluble in potassic sulphate was precipitated with ammoniac oxalate. The precipitate ignited with sulphuric acid, and tested in a radiant matter tube, gave the citron spectrum with great brilliancy.

Certain chemical facts concerning the behaviour of the sought-for element which came out during the course of the tentative trials described in the paper considerably narrowed the list amongst which it might probably be found. All the evidence tends to show that it

belongs to the group of earthy metals, consisting of aluminium, beryllium, thorium, zirconium, cerium, lanthanum, didymium, and the yttrium family, together with titanium, tantalum, and niobium. The sought-for earth is insoluble in excess of potash; this excludes aluminium and beryllium. It is not precipitated by continued boiling with sodic thiosulphate; this excludes aluminium, thorium, and zirconium. Fused with acid potassic sulphate, the resulting compound is readily soluble in cold water; this excludes tantalum and niobium. Evaporating to dryness with hydrochloric acid and heating for some time does not render the mass insoluble in water; this excludes titanium and silicium. It is easily soluble in an excess of a saturated solution of potassic sulphate; this excludes thorium, the cerium group, some of the numerous members of the yttrium group, and zirconium. The only remaining elements among which this elusive body would probably be found are those members of the yttrium family which are not precipitated by potassic sulphate.

The yttria earths form a somewhat numerous family. Fortunately for chemists, a mineral rich in yttria earths—samaraskite—has been found lately in large quantity in Mitchell County, North Carolina, and to this mineral I accordingly now directed my attention.

The following list of elements of the yttrium and its allied families said to occur in samarskite and similar minerals may be considered complete to the present time.

| Name.                      | Absorption spectrum. | Hydrogen equivalent of metal.*<br>(Type of oxide $M_2O_3$ .) |
|----------------------------|----------------------|--------------------------------------------------------------|
| Cerium . . . . .           | No . . . . .         | 47.1                                                         |
| Decipium . . . . .         | Yes . . . . .        | 57.0                                                         |
| Didymium . . . . .         | Yes . . . . .        | 48.5                                                         |
| Didymium $\beta$ . . . . . | Yes . . . . .        | 47.0                                                         |
| Erbium . . . . .           | Yes . . . . .        | 55.3                                                         |
| Holmium. . . . .           | Yes . . . . .        | 54.0                                                         |
| Lanthanum. . . . .         | No . . . . .         | 46.0                                                         |
| Mosandrum . . . . .        | No . . . . .         | 51.2                                                         |
| Samarium. . . . .          | Yes . . . . .        | 50.0                                                         |
| Scandium . . . . .         | No . . . . .         | 14.7                                                         |
| Terbium . . . . .          | No . . . . .         | 49.5                                                         |
| Thulium . . . . .          | Yes . . . . .        | 56.5                                                         |
| Ytterbium. . . . .         | No . . . . .         | 57.9                                                         |
| Yttrium. . . . .           | No . . . . .         | 29.7                                                         |
| Yttrium $\alpha$ . . . . . | No . . . . .         | 52.2                                                         |
| Yttrium $\beta$ . . . . .  | Yes . . . . .        | 49.7                                                         |

\* As it is at present doubtful whether the oxides of several of the metals in this table belong to the type  $M_2O$ ,  $M_2O_3$ , or  $MO$ , I have, for the sake of uniformity and

Some of these claimants it is certain will not stand the test of further scrutiny. Thus samarium and yttrium  $\beta$  are in all probability identical; and I have not included philippium, as Roscoe has conclusively proved that this is a mixture of terbium and yttrium, and my own results confirm those of Roscoe. Moreover, some of these so-called elements will probably turn out to be mixtures of other known elements. But in the confessedly very imperfect state of our knowledge of the chemistry of these metals it is not safe for me in this research to assume that any one of them will surely not survive. The complete list as it stands will therefore be taken to contain all hitherto claimed as new, although it is almost certain to include too many.

In the second column "Yes" or "No" indicates whether the solutions give an absorption spectrum when examined by transmitted light. After numerous experiments I satisfied myself that the metal giving the citron band spectrum was not one of those giving an absorption spectrum. The possible elements, therefore, became narrowed to the following list:—Cerium, lanthanum, mosandrum, scandium, terbium, thorium, ytterbium, yttrium, yttrium  $\alpha$ , and zirconium.

Of these the potassic sulphate reaction excludes cerium, lanthanum, scandium, thorium, yttrium  $\alpha$ , and zirconium, so there are left only the following:—

Mosandrum,  
Terbium,  
Ytterbium,  
Yttrium.

Certain chemical reactions for a long time made me dismiss yttrium from the list of likely bodies. In my analysis of zircons, towards the latter part of the process, I used the following process to separate the iron:—The solution mixed with tartaric acid and excess of ammonia was allowed to stand for some time. A small quantity of a precipitate gradually formed, which was filtered off, and it was this filtrate, after separating the iron with ammoniac sulphide, that yielded the greatest quantity of substance giving the citron band. Now one of the methods of separating yttria from alumina, beryllia, thoria, and zirconia is to precipitate it as tartrate in the presence of excess of ammonia, the other earths remaining in solution. Fresenius says:—"The precipitation ensues only after some time, but it is complete."

The precipitate thus obtained with tartaric acid and ammonia should therefore contain all the yttria: *it gave no citron band whatever in the radiant matter tube*; whilst the residue, which should be free from

simplicity in calculating the values from the composition of their salts, by which these metals are chiefly discriminated, taken the type of oxide to be  $M_2O$ .

yttria, proved for a long time the only source of material wherewith to investigate the chemical properties of the body giving the citron spectrum.

Another reason which made me at this stage of the research pass over yttria was that I had already tested this earth in the radiant matter tube. In a paper on "Discontinuous Phosphorescent Spectra in High Vacua," read before the Royal Society, May 19, 1881, I said, "Yttria shows a dull greenish light, giving a continuous spectrum."

For these reasons I for a long time omitted yttria from my list of possible bodies, and considered that the earth, if not a new one, might turn out to be either mosandra, terbia, or ytterbia.

About 15 lbs. weight of samarskite was worked up, partly by the hydrofluoric acid method of Lawrence Smith, and partly by fusion with potassic bisulphate.

These methods both gave as a result a large quantity of mixed earths containing most, if not all, the bodies enumerated in the foregoing list. Tested in the radiant matter tube this mixture gave the citron spectrum very brilliantly.

These earths were treated by a series of chemical processes too long and complicated to describe in this abstract, and the result of about five hundred fractional precipitations gave me a mixture of earths having an H equivalent,  $M=48$ , and showing a strong absorption spectrum; a mixture having an H equivalent,  $M=33$ , having no absorption spectrum; and intermediate earths.

In the radiant matter tube all these fractions gave the citron band spectrum well, but that of the earth of lowest equivalent was much the brightest, and that of the highest equivalent the least intense.

Three methods are available for the partial separation of these earths and for the complete purification of any one of them. The formic acid process is best for separating terbia, as terbic formate is difficultly soluble in water, the other formates being easily soluble.

Fractional precipitation with oxalic acid separates first erbia, holmia, and thulia, then terbia, and lastly yttria. This is the only method which is applicable for the separation of small quantities of terbia from yttria.

Fusing the nitrates separates ytterbia, erbia, holmia, and thulia from yttria. It is not so applicable when terbia is present, and is most useful in purifying the gadolinite earths. This process is the only one known for separating ytterbia from yttria.

Selection must be made of these methods according to the mixture of earths under treatment, changing the method as one earth or the other becomes concentrated on one side or thrown out on the other. Each operation must be repeated many times before even approximate purity is attained. The operations are more analogous to the separation of members of homologous series of hydrocarbons by fractional

distillation than to the separations in mineral chemistry as ordinarily adopted in the laboratory.

Pure terbia ignited with sulphuric acid and tested in the radiant matter tube shows no citron band spectrum. A concentrated solution of the purest terbia obtained in this way, when examined by the spectroscope, showed no absorption lines whatever: proving the absence of erbium, holmium, and thulium.

I did not attempt any separation of erbium, holmium, and thulium from each other, as the evidence obtained was sufficient to show that the element giving the citron band spectrum was not one of these three metals. Likewise I had far too little material to enable me to enter on a work of such difficulty with any prospect of success.

The chemical characters of mosandra are so little known that I could not attempt to search for it. But as the citron band-forming earth always appeared concentrated amongst those whose double sulphates were most soluble in potassic sulphate—and, of these, amongst those having the palest colour and lowest atomic weight—it was scarcely conceivable that the earth I was in search of should ultimately prove to be one whose properties did not in any case correspond to these—of a dark orange-yellow colour, forming a difficultly soluble double potassic sulphate, and having the very high equivalent of  $M=51.2$ ; these being the properties ascribed to mosandra by the discoverer, Professor Lawrence Smith.

Ytterbia was prepared from gadolinite, as this mineral is said by Nilson to contain most ytterbia. It was separated from accompanying earths by processes described in the paper. The resulting earth gave at first a faint citron band spectrum, evidently due to impurity; on repeating the purification several times I at last succeeded in obtaining a white earth which gave only the merest trace of citron band spectrum. Its hydrogen equivalent, 58.0, and its chemical properties showed that it was probably Marignac's ytterbia. Subsequent experiments satisfied me that this earth did not contain more than  $\frac{1}{10000}$  part of yttria. The extreme tediousness of the chemical operations necessary to obtain this high degree of purity, and the long time they required, prevented me from pushing these results beyond what was necessary to prove the special point at issue.

The yttria, purified as already described, might still contain traces of terbia, together with erbia, holmia, and thulia. These were gradually removed by the fusing nitrate process. The atomic weight gradually got down to 31.0, but the spectra did not vary very much; that from the earth of lowest atomic weight being, however, the most brilliant.

Pure yttria is quite white. That from gadolinite on testing in the radiant matter tube gave a spectrum absolutely identical with that given by the zircon, cerite, thorite, orangite, and samarskite yttria.

Pure yttria was also prepared from ytthro-tantalite, euxenite, tyrite, and also from plaster of Paris and common limestone. In no case could I detect any difference in the position or intensity of the lines shown by their phosphorescent spectra.

*The Phosphorescent Spectrum of Yttria.*

The spectrum shown by pure ignited yttric sulphate in a radiant matter tube is one of the most beautiful objects in the whole range of spectroscopy. The spectrum is best seen under low dispersion and not too narrow a slit. It consists essentially of a broad red band, an intensely brilliant citron band, and two almost equally brilliant green bands. Other fainter lines are also seen, but they are not characteristic. Coloured drawings and maps of the spectrum to scale accompany the paper. This description applies to the spectrum shown either by pure yttric sulphate or by an earth tolerably rich in yttria. When traces are present the citron band only is seen. A little more yttria brings out the first and then the second green band, and finally, as the proportion of yttria increases, the red and blue bands appear.

The paper next gives a description of experiments made with pure yttria, and with various compounds of it, to see which would give the most characteristic spectrum. The sulphate heated to redness was found to give the best results. Pure yttria precipitated by ammonia did not phosphoresce in the slightest degree, and, necessarily, no citron band spectrum was to be seen. The yttria was removed from the tube, converted into sulphate, heated to redness, and again tested. This time it gave the citron band magnificently. This shows what apparently trivial circumstances will alter the whole course of an investigation. In 1881, when searching for discontinuous phosphorescent spectra, I tried a similar experiment with pure precipitated yttria, and entirely missed its citron band spectrum. Had I first treated the yttria with sulphuric acid instead of testing the earth itself in the radiant matter tube the results would have been very different, and this research would probably have never been undertaken.

Yttria was now prepared by igniting the precipitated oxalate at a red heat. On testing it in the radiant matter tube it phosphoresced with feeble intensity, the light being about one-twentieth of that given by the ignited sulphate under similar conditions. The citron band was almost as sharp as the sodium line, and was shifted one division towards the blue end. The two green bands were visible, but very hazy and indistinct, and only to be resolved into bands with difficulty.

It is an old and probably a true saying that every element could be detected everywhere had we sufficiently delicate tests for it. Early observations had prepared me for the wide distribution of the element

giving the citron spectrum, and no sooner had the exquisite sensitiveness of this spectrum test forced itself on my notice than I sought for yttrium in other minerals. The facts which I had noticed in connexion with the variation of the appearance of the citron spectrum, according to the quantity of yttrium present, showed that it might be possible to devise a process for the rough quantitative estimation of yttrium, and after several experiments a spectrum test was devised sufficiently delicate to detect one-millionth part of yttria in a mineral. A table is given showing the results of this quantitative spectrum analysis, from which it is seen that amongst other substances a specimen of coral contains one part of yttrium in 200 parts; strontianite, one part of yttrium in 500 parts; chondrodite, from Mount Somma, one part in 4,000; calcite, one part in 10,000; ox bone, one part in 10,000; an earthy meteorite (Alfianello), one part in 100,000; and tobacco ash, one part in 1,000,000.

The following Paper was read:—

“Experiments upon the Heart of the Dog with reference to the Maximum Volume of Blood sent out by the Left Ventricle in a Single Beat, and the Influence of Variations in Venous Pressure, Arterial Pressure, and Pulse Rate upon the Work done by the Heart.” By WILLIAM H. HOWELL, A.B., Fellow of the Johns Hopkins University, and F. DONALDSON, Jr., A.B. Communicated by Dr. M. FOSTER, Sec. R.S.

(Abstract.)

Owing to the indirectness of the methods hitherto used for estimating the quantity of blood pumped out from the left ventricle at each systole, this important factor in all calculations of the work done by the heart has never been satisfactorily determined. Of the later physiologists who have investigated the subject, Volkmann and afterwards Vierordt, from calculations based upon the mean velocity of the stream of blood in the unbranched aorta, obtained the fraction  $\frac{1}{4000}$  as representing the ratio of the average weight of blood ejected at each systole of the left ventricle to the weight of the whole body. Fick, from data obtained by placing the arm in a plethysmograph, and estimating the velocity of the stream of blood in the axillary artery from the increase in volume of the whole arm at each systole of the heart, arrived at a much smaller fraction, about  $\frac{1}{10000}$ , for the ratio between the weight of blood thrown out at each systole and the body-weight.